Development of Surrogate Model Fuel for F-76

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Outline of talk

- ONR project
- Surrogate model for F-76 diesel fuel
  - Physical property model for F-76
  - Reaction kinetics model for F-76
- Summary and Conclusions
- Future work

UW - ONR project

"Development of Assessment Methods for Alternative Fuels for Naval Diesel Engines"

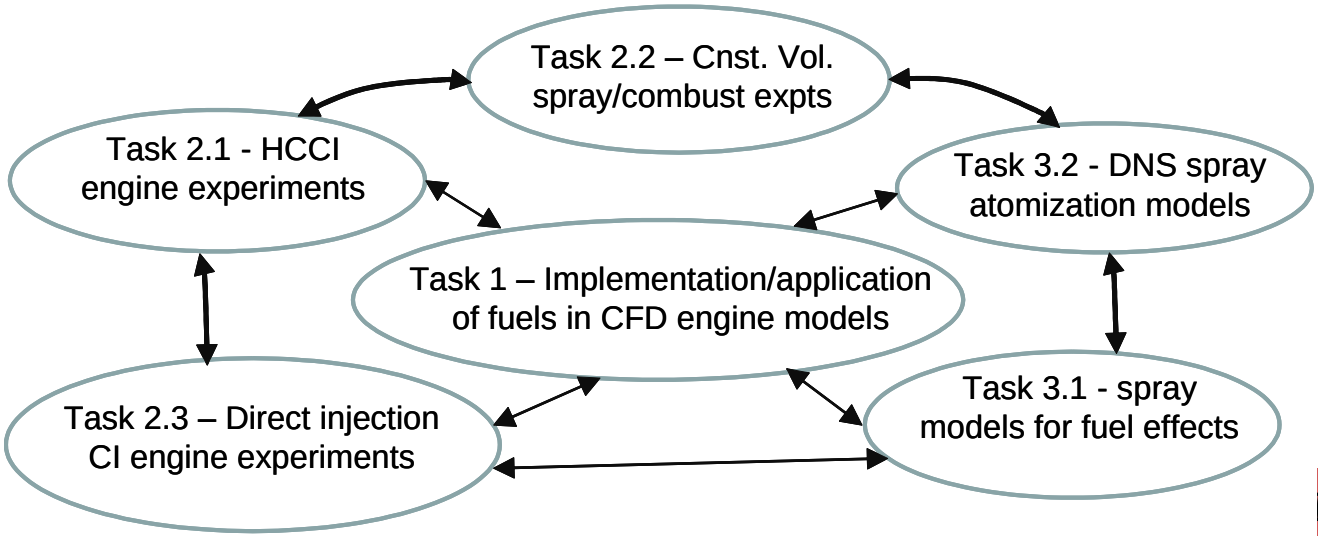
Focus:

Understanding physical effects of incorporating alternative fuels into Naval systems. Identifying fuel characteristics needed for acceptable operation of current diesel engines deployed by the Navy and Marine Corps.

Research goals:

a.) Development and validation of modeling/simulation tools that predict engine performance/degradation using wide variety of alternative fuels.

b.) Increasing the knowledge of physical properties and chemical reactions of alternative fuels in a maritime environment.



Task1 of project

- Develop physical property models for baseline F-76 fuel
- Development of PSGCR kinetics model.
- Modeling of HCCI engine ignition experiments (Task 2.1)
- Modeling of ignition experiments (Task 2.2)
- CFD simulation of engine combustion/spray behavior.

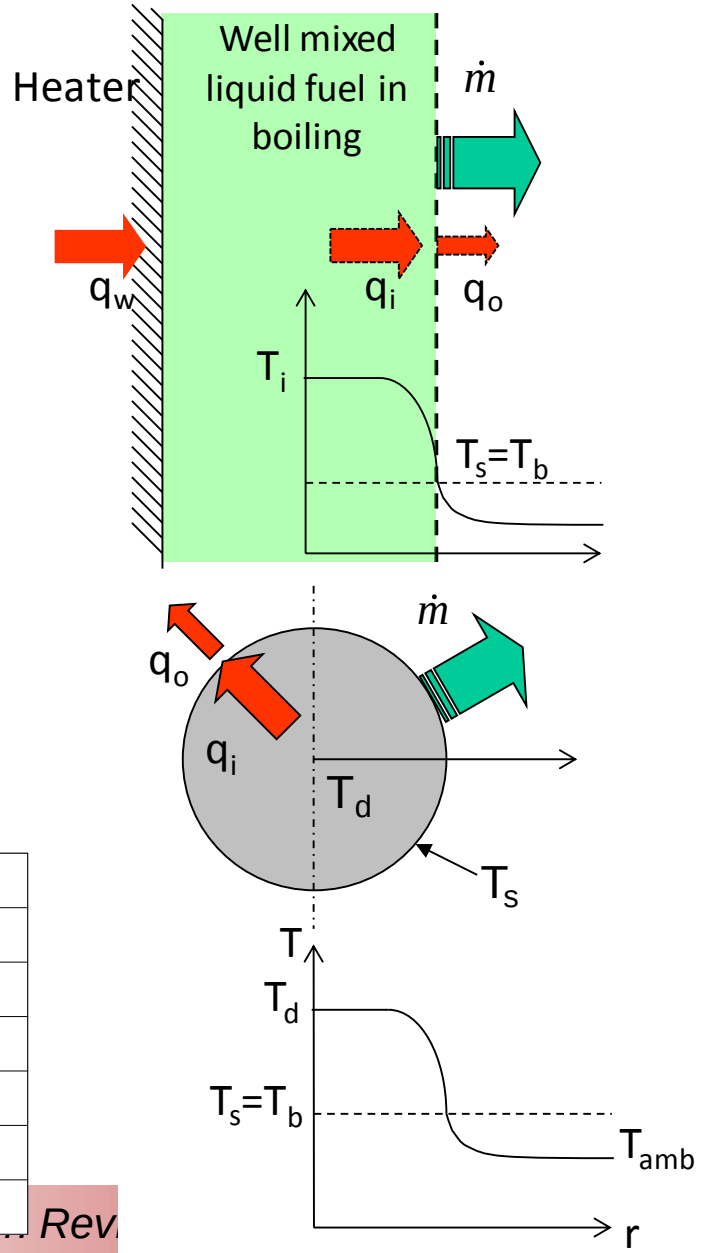
Surrogate fuel model for F-76

Physical property model for F-76

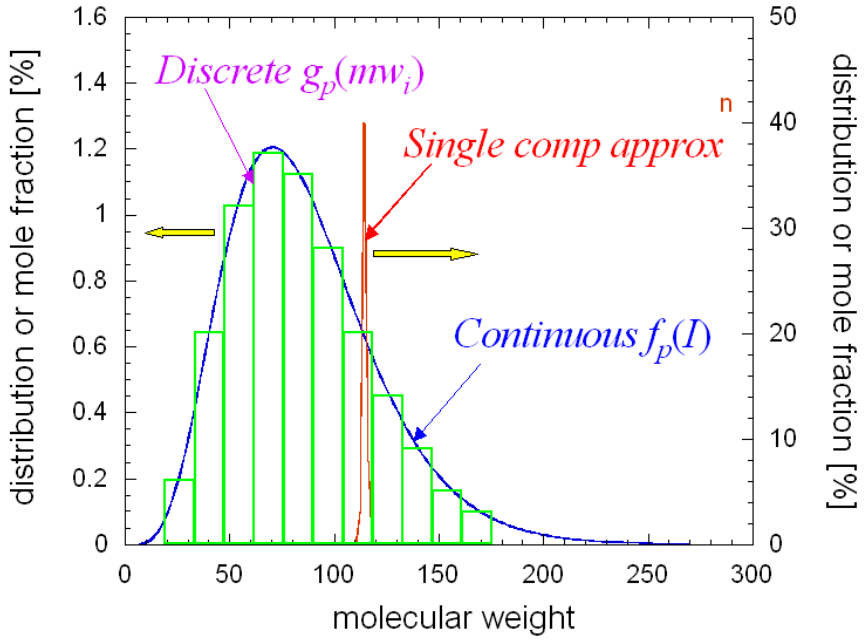
Methodology

- Fuels are modeled as mixtures of surrogate components whose properties are calculated using a discrete multi-component (DMC) model (32 components).
- Surrogate components and their composition are chosen to match measured distillation profiles and properties of the target fuel.
- Distillation profiles are obtained by calculating evaporation history of a single drop in boiling condition.
- Properties of a mixture are calculated from the properties of individual pure components using appropriate equations.

No.	Physical property	No.	Physical property
p1	**Liquid density**	p7	**Vapor heat capacity**
p2	**Vapor pressure**	p8	**Vapor diffusivity**
p3	**Surface tension**	p9	**Vapor viscosity**
p4	**Liquid viscosity**	p10	**Vapor thermal conductivity**
p5	**Liquid thermal conductivity**	p11	**Liquid Heat capacity**
p6	**Heat of vaporization**	p12	**Critical properties**



Discrete multi-component fuel model



Chemical class	Fuel component
n-Alkanes (10)	C5 ~ C21
iso-Alkanes (4)	iC_5H_{12}, iC_8H_{18}, $iC_{10}H_{22}$, $iC_{16}H_{34}$
Olefins (4)	C_8H_{16}, C_7H_{14}, C_6H_{12}, C_5H_{10}
Naphthenes (3)	Cyclohexane, Methylcyclohexane, Decalin
Aromatics (11)	Benzne, Toluene, Heptylbenzene, Hexylbenzene, Pentylbenzene, iso-Propylbenzene, mXylene, mCymene, Tetralin, Naphthalene, Phenanthrene

Discrete Multi-Component

- Discrete system of a liquid phase + Discrete mixture system of vapor phase fuel and ambient gas:

$$G_p(I) = \sum_{F=1}^{N_F} x_F{}^p \delta(I - I_F) + \sum_{s=1}^{N_s} x_s{}^p \delta(I - I_s)$$

discrete phase of fuel

discrete phase of air/fuel mixture

- Vapor phase transport equation,

$$\frac{\partial}{\partial t}[\rho y_i] + \nabla \cdot [\rho y_i v] = \nabla \cdot (\rho D_i \nabla y_i) + s_{g,i}$$

$$\sum \Rightarrow$$

$$\frac{\partial}{\partial t}[\rho y_F] + \nabla \cdot [\rho y_F v] = \nabla \cdot (\rho \bar{D} \nabla y_F) + S_g$$

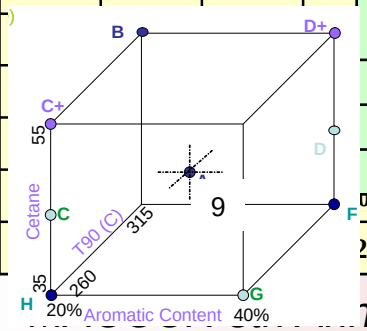
(Ra and Reitz, 2009)

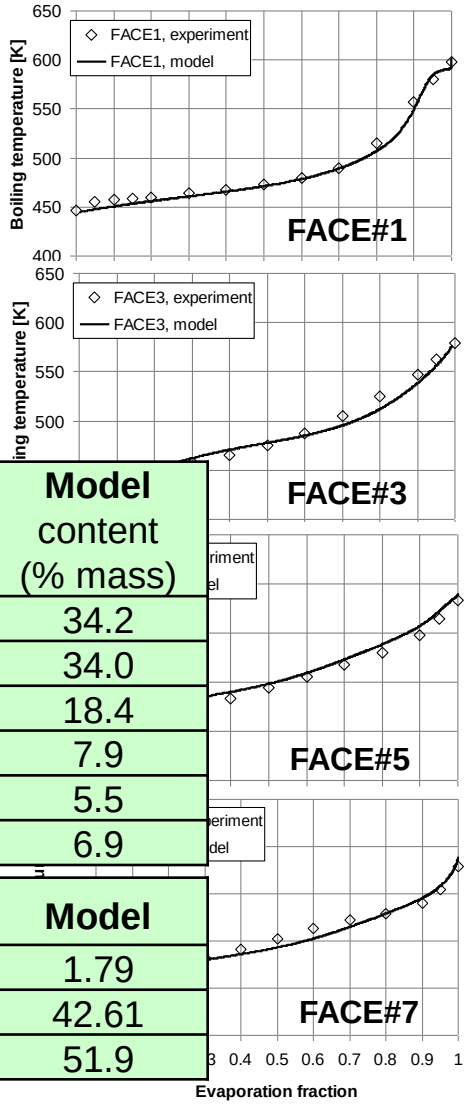
Application of DMC model to FACE fuels

Surrogate Hydrocarbons	Molecular Formula	Surrogate mass fractions of FACE fuels								
		1	2	3	4	5	6	7	8	9
n-decane	c10h22(PC)					0.100		0.161		0.050
n-dodecane	c12h26(PC)	0.162	0.090					0.090	0.027	
n-tridecane	c13h28(PC)				0.050	0.166				
n-tetradecane	c14h30(PC)				0.000	0.130	0.099	0.100	0.169	0.050
n-hexadecane	c16h34(PC)			0.080	0.050	0.060	0.198	0.102	0.122	0.181
n-octadecane	c18h38(PC)	0.101	0.020	0.040	0.070	0.071	0.091	0.041	0.051	
n-eicosane	c20h42(PC)		0.050							0.061
n-heneicosane	c21h44(PC)		0.050		0.080		0.080		0.046	
2,2,3,3 tetramethylhexane	c10h22(IP)	0.260	0.367	0.095	0.0					
2,2,4,4,6,8,8 heptamethylnonane	c16h34(IP)	0.100	0.070	0.100	0.1					
cyclohexane	c6h12(MCP)	0.030	0.030	0.050	0.0					
decalin	c10h18(DCP)	0.120	0.120	0.200	0.1					
m-xylene	c8h10(AB)		0.010	0.020						
tetralin	c10h12(AB)	0.008	0.007	0.075	0.0					
naphthalene	c10h8(PA)	0.015	0.012	0.058						
anthracene	c14h10(PA)				0.0		0.050		0.169	0.055
m-cymene	c10h14(AB)									
n-pentylbenzene	c11h16(AB)									
n-hexylbenzene	c12h18(AB)									
n-heptylbenzene	c13h20(AB)								0.030	0.098	0.160	0.070	0.124
Number of surrogate species						2	14	9	12	12	12

FACE #9 Hydrocarbon type	Measured content (% mass)	Model content (% mass)
Paraffins	34	34.2
Total napthenes	34	34.0
Alkylbenzenes	18.2	18.4
Mono aromatics	8.2	7.9
Poly aromatics	5.5	5.5
Tetralins	6.9	6.9

Property	Measured	Model
H/C ratio	1.79	1.79
LHV (MJ/kg)	42.44	42.61
Cetane Number	45.0	51.9



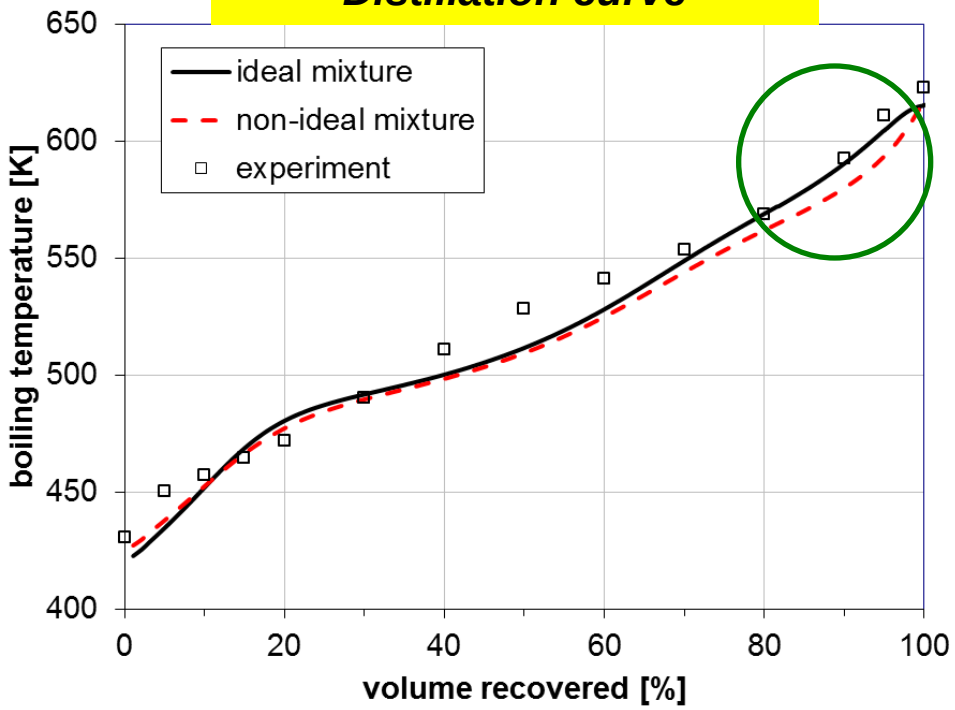


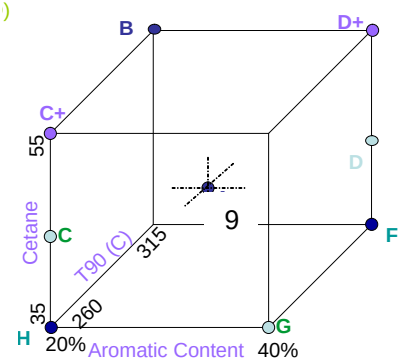
Krishnasamy, Ra, Reitz and Bunting – Energy & Fuels 2011

Activity Coefficients of Face #9 Surrogates

Component	Chemical structure	Activity coefficient γ at 373 K
n		1.01
		0.88
		1.03
		1.06
n		0.95
		0.81
F		2.22
		1.06
		1.07
P		1.08
Tetralin ($C_{10}H_{12}$)		1.17
Heptylbenzene ($C_{13}H_{20}$)		1.10

Distillation curve





UNIFAC Model

Departure from Raoult's law - Non-ideal vaporization influences heavy-end of distillation curve *

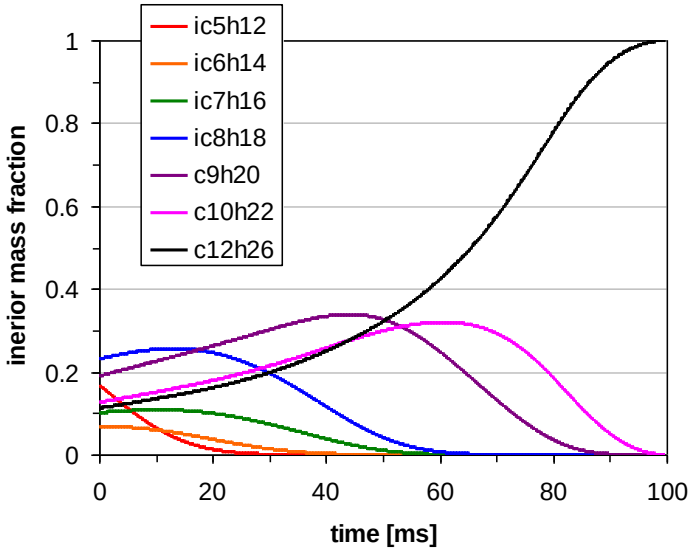
$$p_{i,v} = x_{i,v}P$$

$$= x_{i,l}\gamma_i P_{sat,i}$$

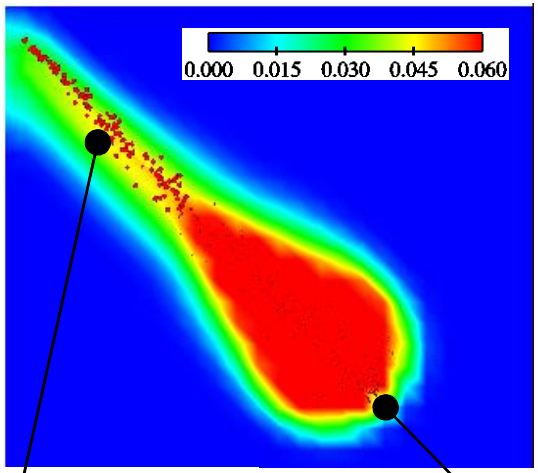
* Krishnasamy, Ra, Reitz and Bunting – Energy & Fuels 2011

Multi-component fuel vaporizing sprays

Single drop vaporization

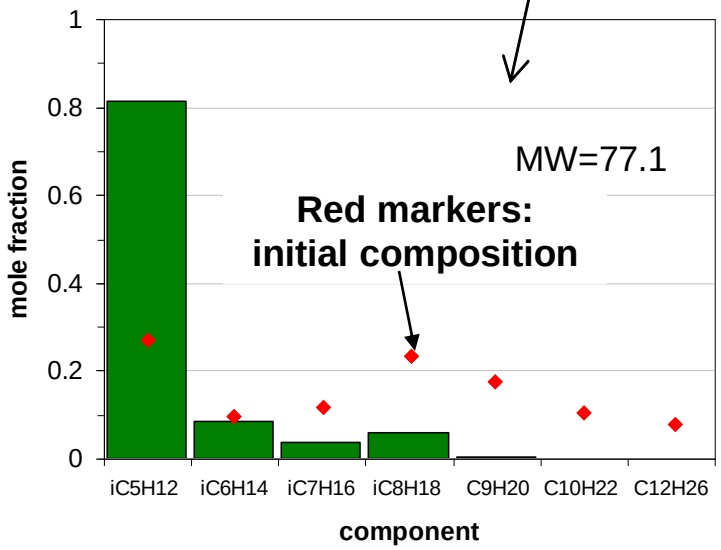


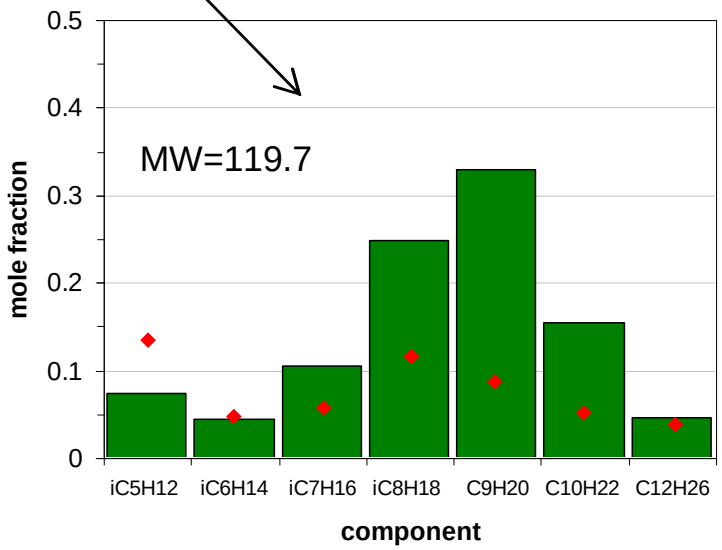
Total fuel mass fraction distribution



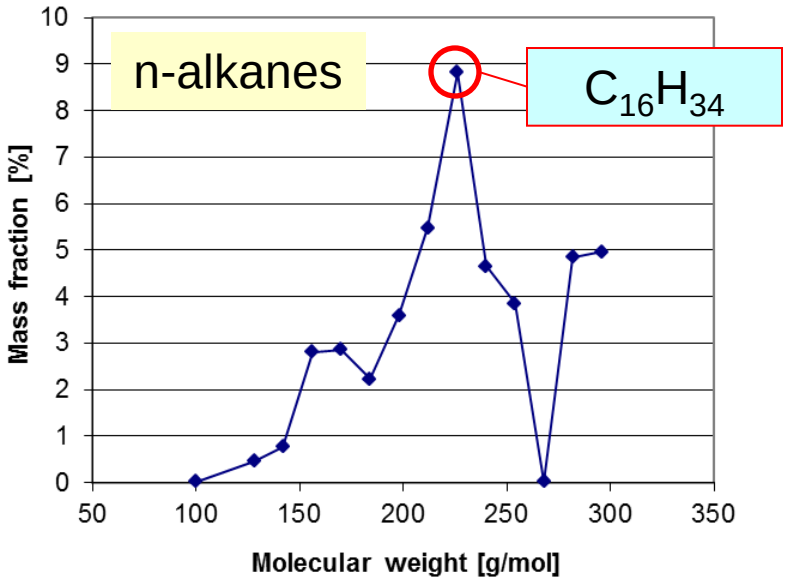
Gasoline
7-components
Do=30 μm
Vinj=100 m/s

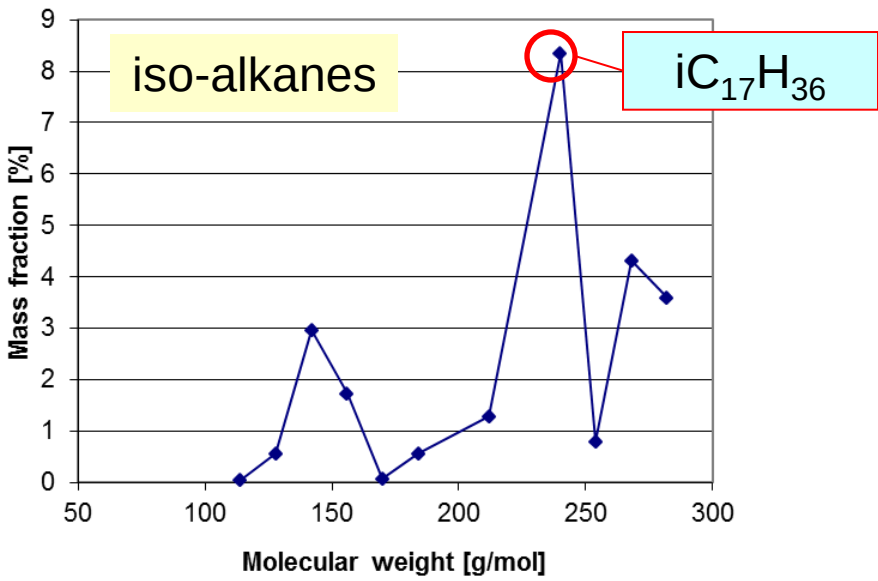
@ 2.0 ms after SOI

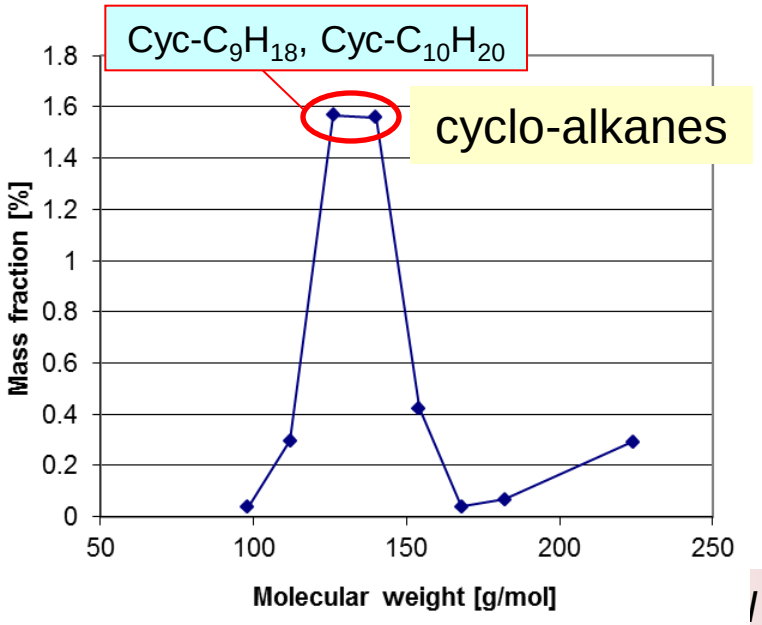


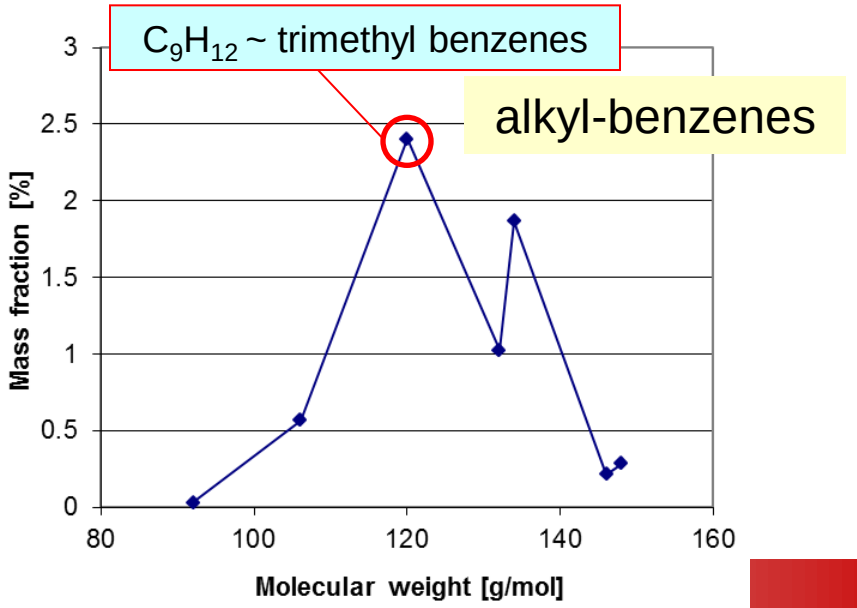


Measured composition of F-76







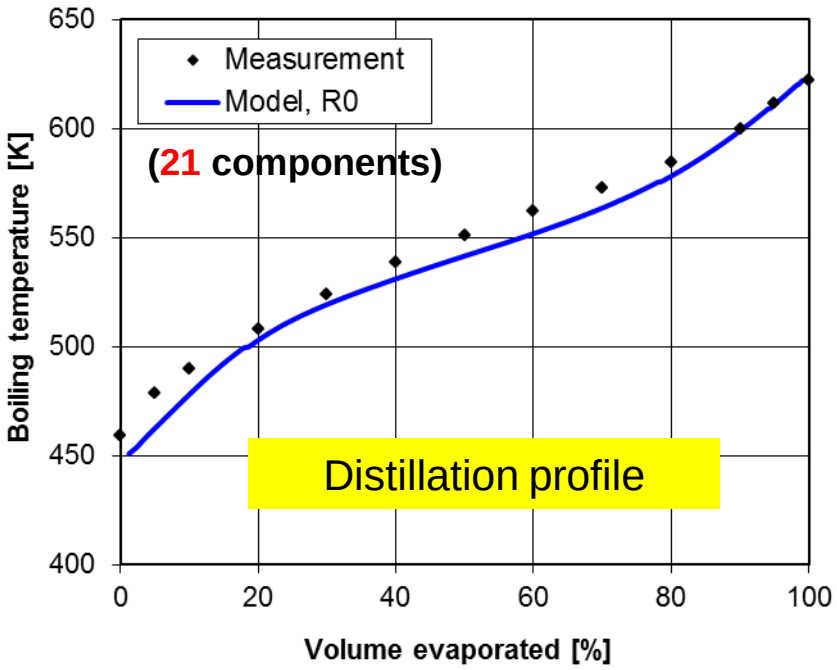


l Fuels

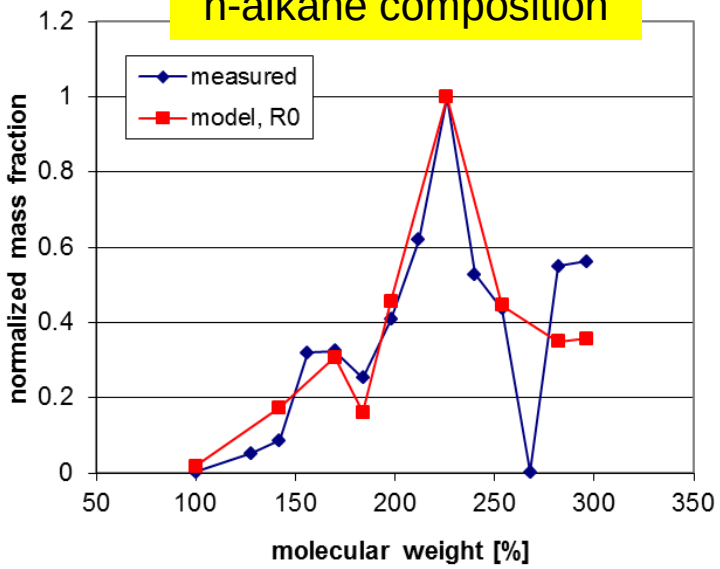
Model composition of F-76

Fuel composition

Class	Mass fraction		
	Measured	C-range	Model, R0
n-alkane	50.50	C9~C21	59.94
i-alkane	25.38	C8~C20	25.94
mono-naphthene	4.53	C7~C16	4.71
poly-naphthene	0.44	C11	0.46
mono-aromatic	6.39	C7~C11	6.31
poly-aromatic	0.84	C12	0.88
tetralin	1.52	C10~C11	1.58
alkene	1.66	C9~C19	1.76
oxygenated	5.87	C9~C20	0
other	3.61	C9~C20	0



n-alkane composition

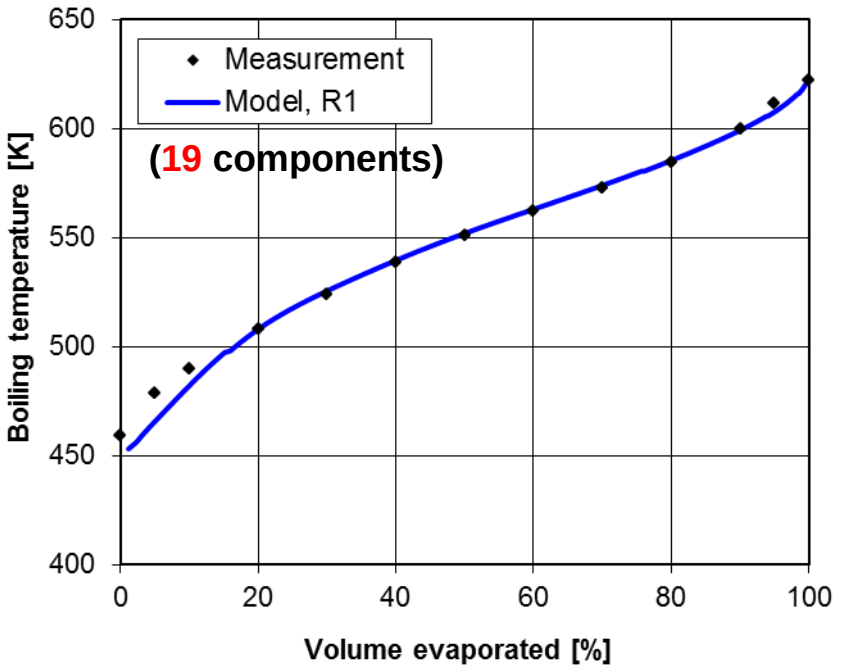


- For the current surrogate model, the contents of Oxygenate and Other are added to n-alkanes proportionally.
- Oxygenates are mostly alcohols ($C_{16}H_{34}O$) and ketones ($C_{10}H_{16}O$).

➔ to be considered in the future (*non-ideal mixture model-UNIFAC*).

Model composition of F-76

Class	Mass fraction			
	Measured	C-range	Model, R0	Model, R1
n-alkane	50.50	C9~C21	59.94	56.6
i-alkane	25.38	C8~C20	25.94	26.4
mono-naphthene	4.53	C7~C16	4.71	4.7
poly-naphthene	0.44	C11	0.46	0.5
mono-aromatic	6.39	C7~C11	6.31	8.6
poly-aromatic	0.84	C12	0.88	1.4
tetralin	1.52	C10~C11	1.58	1.6
alkene	1.66	C9~C19	1.76	1.8
oxygenated	5.87	C9~C20	0	0
other	3.61	C9~C20	0	0

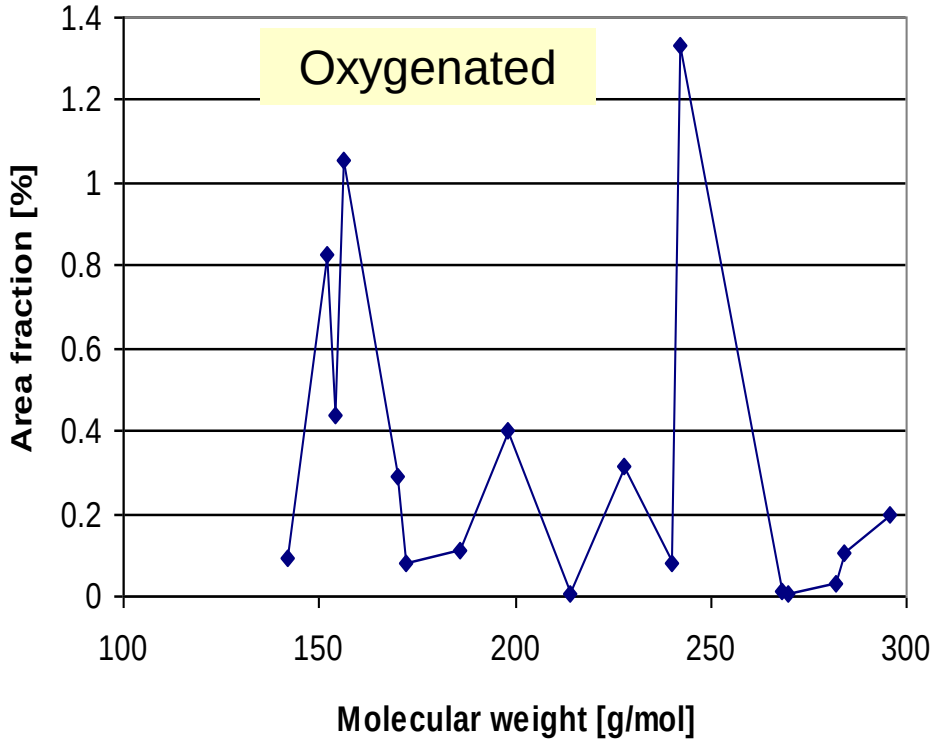


- With slight adjustment of composition and number of species, a better agreement was obtained.

➔ Automation of the process is desirable.

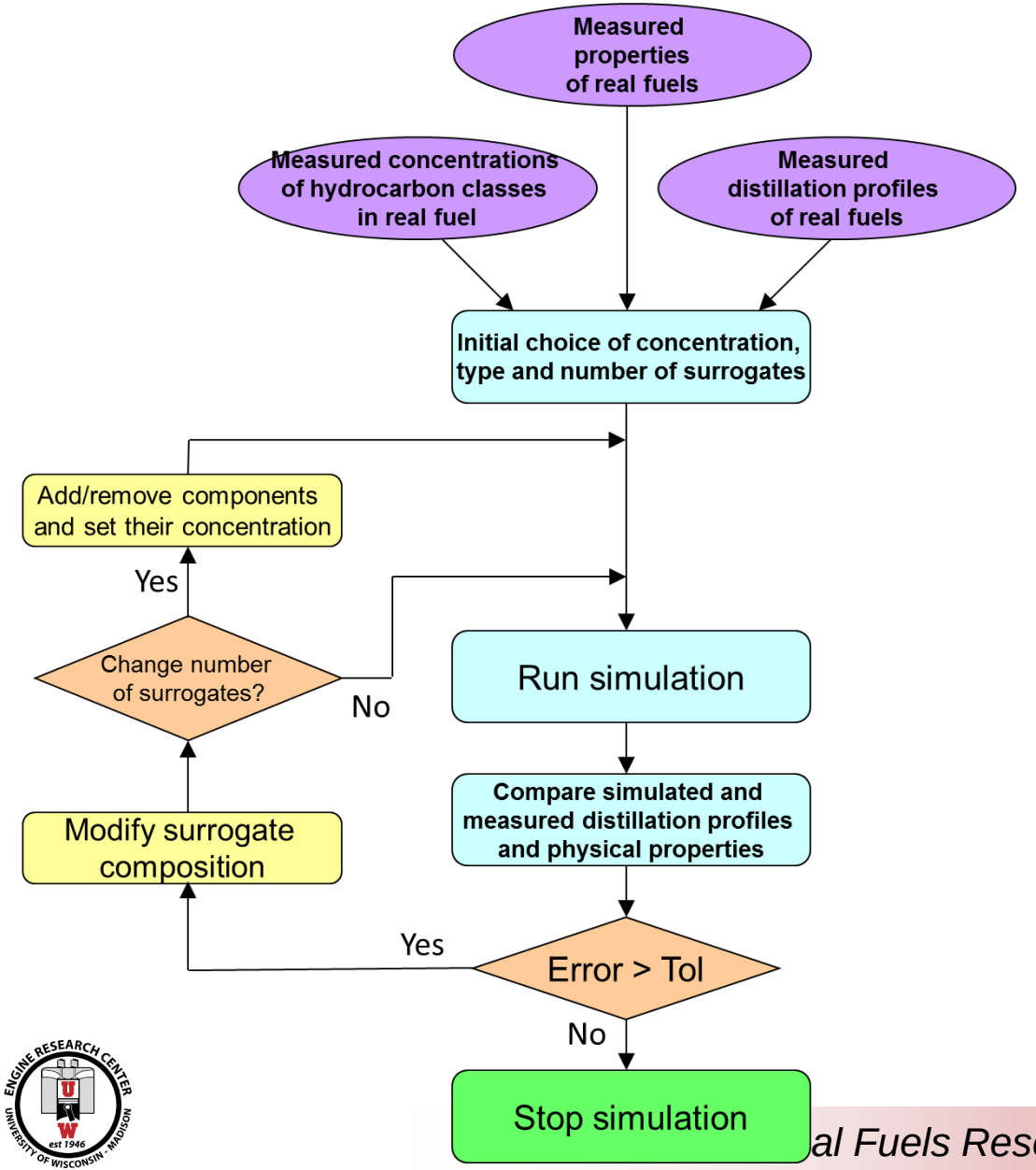
Property	Measured	Model, R0	Error [%] of R0	Model, R1	Error [%] of R1
Density [g/cm^3] at 15C	0.845	0.785	-7.1	0.789	-6.6
Viscosity [cSt] at 40C	3	2.12	-29.5	2.27	-24.2
Surface tension [dynes/cm] at 20C	28	26.57	-5.1	26.83	-4.2
LHV[MJ/kg]	42.6	44.07	3.5	43.95	3.2
H/C [mol ratio]		2.05		2.03	
Hydrogen content[%]	13.2	14.6	10.6	14.47	9.6
MW[g/mol]		191.6		196.5	
CN	51	60.14	17.9	58.04	13.8

Oxygenated components in F-76



Formula	MW	Area_fraction [%]	Species name	Class
$C_{10}H_{16}O$	152	0.825	4,7,7-trimethyl- bicyclo[4.1.0]heptan-3-one	ketone
$C_{10}H_{18}O$	154	0.436	3-butyl- cyclohexanone	ketone
$C_{10}H_{20}O$	156	1.055	5-methyl-2-(1-methylethyl)- cyclohexanol	alcohol
$C_{13}H_{26}O$	198	0.398	cyclododecanemethanol	alcohol
$C_{16}H_{34}O$	242	1.33	2-hexyl- 1-decanol	alcohol

Automation of fuel modeling process



Target properties:

- Distillation profiles
- Specific gravity
- Viscosity
- Surface tension
- Lower heating value (LHV)

Hydrogen to carbon (H/C) ratio

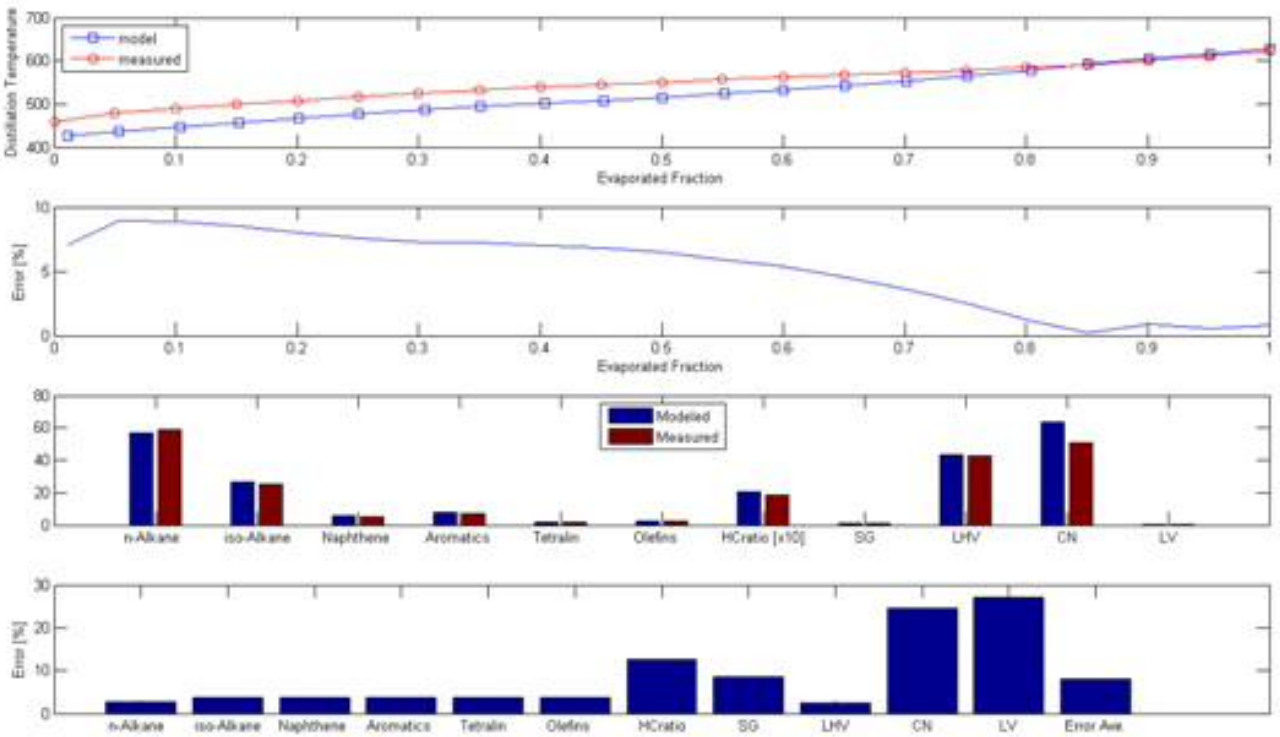
- Contents of chemical classes
- Cetane number

➢User inputs are used as constraints.

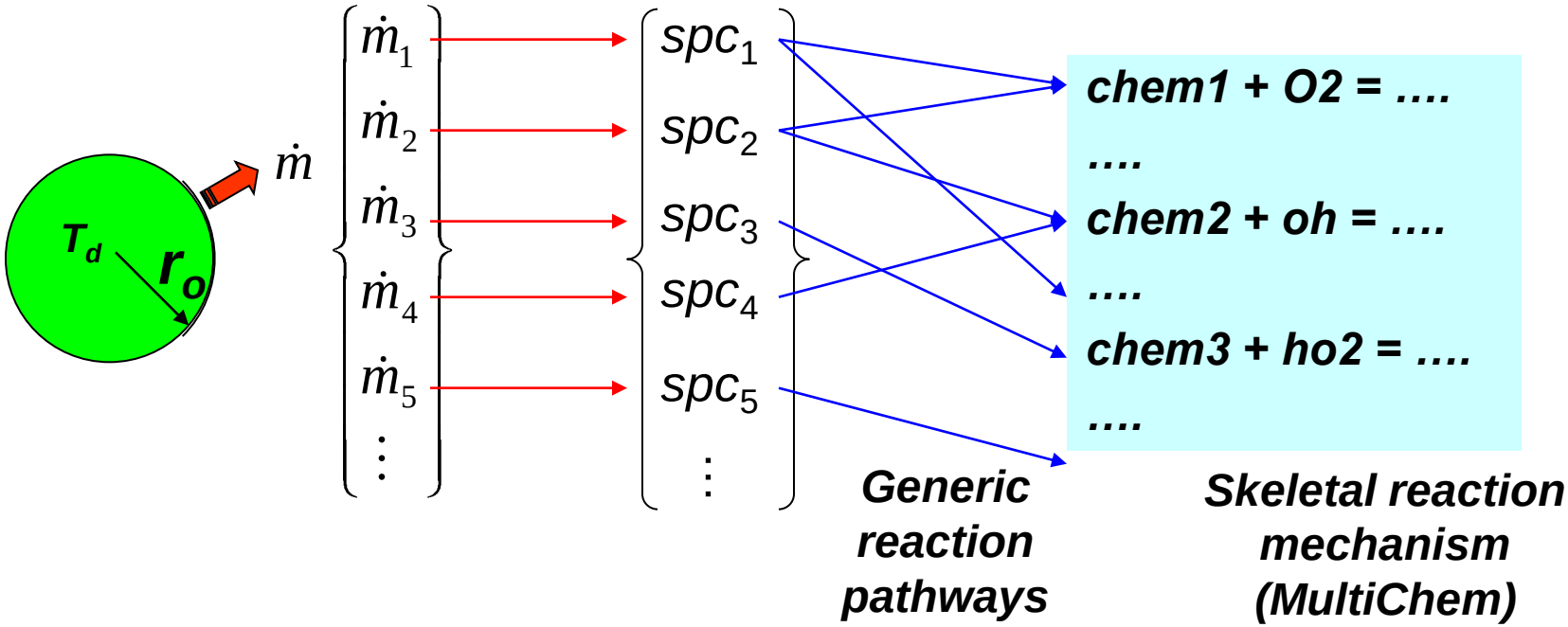
➢Sensitivity of property variation to composition change is obtained in each generation and used in the next generation to modify the model composition.

Test of automatic surrogate search

- Starting composition: Even (arbitrary) distribution of mass fraction of surrogate components in n-alkane, iso-alkane, olefin, naphthene and aromatic classes. (➔ 16 components)
- Matching tolerance (inputs) for each property may be different.
- 13 generations were simulated to match the measured distillation profile.



Physical Surrogate Group Chemistry Representation (PSGCR)



- Reaction pathways of base surrogate components (chem1, chem2, …) represent reaction characteristics of a chemical class (GCR)
- The reactivity of physical surrogate components is captured by the generic reactions connecting the PSC and the base chemical surrogate components (CSC).

PSGRC: generic reactions for $C_{21}H_{44}$

No.	Reaction	A	n	Ea
1	c21h44+h=c14h29+c3h6+c4h8+h2	1.20E+13	0.0	8400.0
2	c21h44+h=c14h30+c7h15-2	1.20E+13	0.0	8400.0
3	c21h44+oh=c14h29+c3h6+c4h8+h2o	2.70E+13	0.0	-630.0
4	c21h44+oh=c14h30+c6h13+ch2o	5.06E+08	1.0	2870.0
5	c21h44+ho2=c14h29+c3h6+c4h8+h2o2	1.00E+11	0.0	16000.0
6	c21h44+ho2=c14h30+c6h13+hco+oh	1.00E+11	0.0	14000.0
7	c21h44+o2=c14h29+c3h6+c4h8+ho2	6.00E+12	0.0	32600.0
8	c21h44+o2=c14h30+c6h13+hco+o	5.20E+11	0.0	34600.0
9	c21h44+o=c14h29+c3h6+c4h8+oh	1.20E+10	0.0	3000.0
10	c21h44+o=c14h30+c6h13+hco	1.20E+10	0.0	3000.0
11	c21h44=c14h29+c7h15-2	2.00E+17	0.0	87000.0

- Reaction characteristics employed:
H-abstraction, radical decomposition, olefin formation, carbonyl (aldehyde) formation, active radical reproduction (OH, O, HO_2), unimolecule decomposition
- Reaction rate constants were first borrowed from similar reactions in detailed mechanism and then adjusted to give ignition delay times matching available experimental data or known CN behavior.

Type-1 (13 components): c12h26, c13h28, c10h22, c16h34, c18h38, c20h42, c21h44, ic10h22, c13h20, c12h18, c11h16, mcymene, ic9h12(isopropylbenzene),

PSGRC for F-76

Type-2: mXylene
Type-3: iC16H34 (HMN)
Type-4: Tetralin
Type-5: Naphthalene (C10H8)
Type-6: PAH cascade

35 surrogate component data base
(194 species, 877 reactions)

Type-6: PAH cascade

HC + H => HC* + C4H4
HC + H2 => HC* + C4H3
HC + OH => HC* + C2H2 + HCCO
HC + HO2 => HC* + C2H + HCCO + OH
HC + O2 => HC* + C2H + HCCO + O
HC + O => HC* + C2H + HCCO
HC => HC* + C2H + C2H

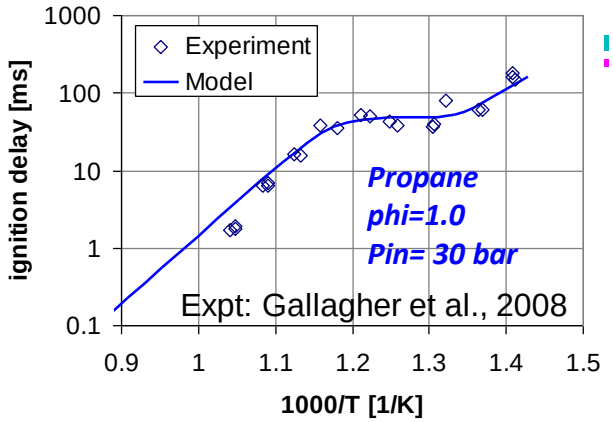
HC: PAH components
HC*: one-ring-less PAH components

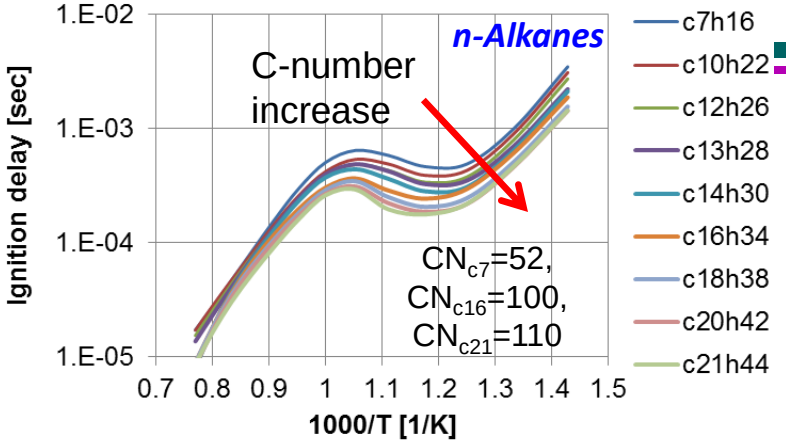
Chemical class	Fuel component	
n-Alkane	Base (6)	c14h30, nc7h16, nc6h14, nc5h12, c4h10, c3h8
	Extended (7)	c10h22, c12h26, c13h28, c16h34, c18h38, c20h42, c21h44
iso-Alkane	Base (2)	ic8h18, ic5h12
	Extended (2)	ic16h34, ic10h22
Olefin	Base (4)	c7h14, c6h12, c5h10, c4h8
	Extended	
Naphthene	Base (3)	Cyclohexane(CHX), Methylcyclohexane(MCH), Decalin(c10h18)
	Extended	
Aromatic	Base (2)	toluene, benzene
	Extended (9)	Heptylbenzene(c13h20), Hexylbenzene(c12h18), Pentylbenzene(c11h16), iso-Propylbenzene(ic9h12), mXylene, mCymene, Tetralin, Naphthalene(c10h8), Phenanthrene(c14h10)

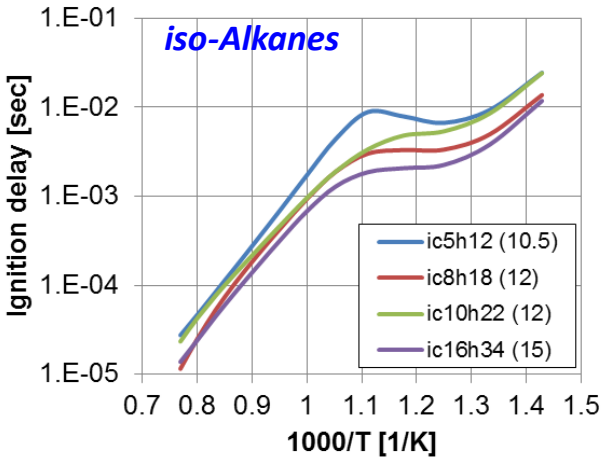
- More extended components should be added to model combustion of heavier olefins and naphthenes, as well as heavy oxygenated fuel (alcohols) in the future.

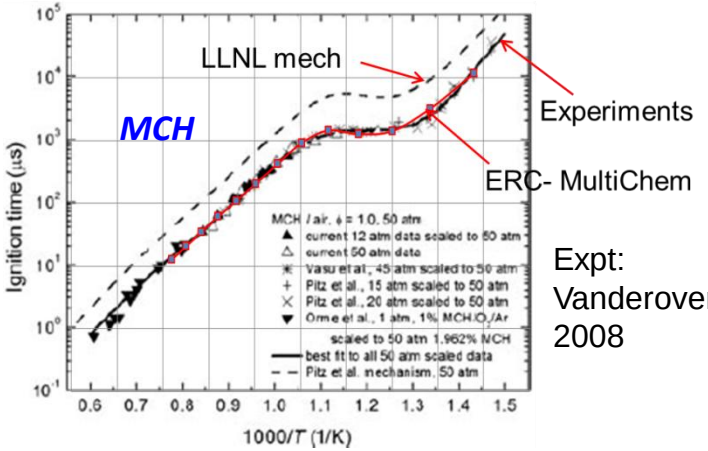
Reaction kinetics model for F-76

Component	Model, R0 mass fraction
ic5h12	0
c5h10	0
nc5h12	0
c6h12	0
nc6h14	0
chx	0
c7h14	0
nc7h16	0.003392
ic8h18	0.000440
mch	0.047096
c7h8	0
c8h16	0.017554
mxylene	0
ic9h12	0
ic10h22	0.055656
c10h22	0.031780
mcymene	0.012754
c10h18	0.004612
c12h18	0.012754
c11h16	0.021796
tetralin	0.015830
c12h26	0.056447
c10h8	0.005588
c13h28	0.029471
c13h20	0
ic16h34	0.197714
c14h30	0.083634
c16h34	0.183337
c18h38	0.081714
c14h10	0.008777
c20h42	0.064088
c21h44	0.065566

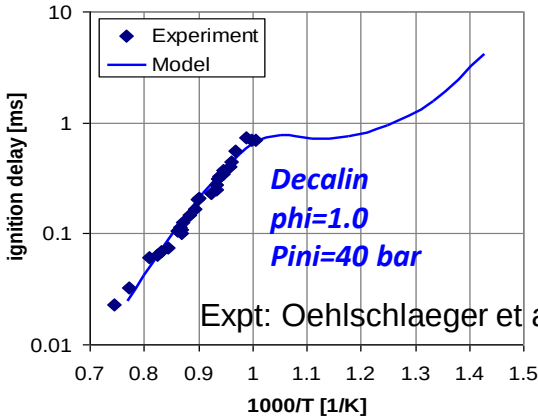


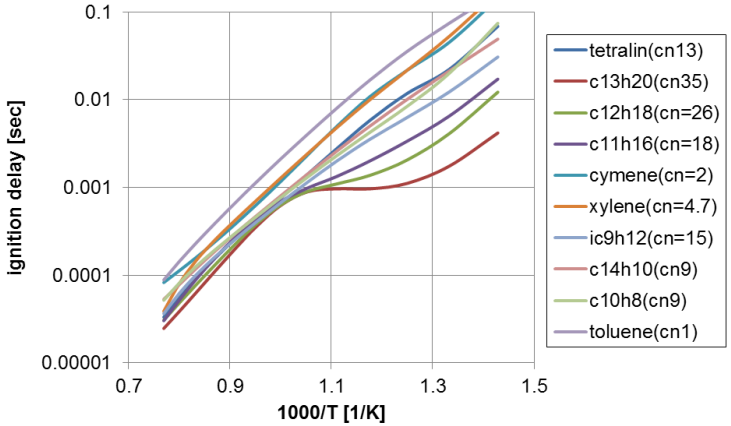






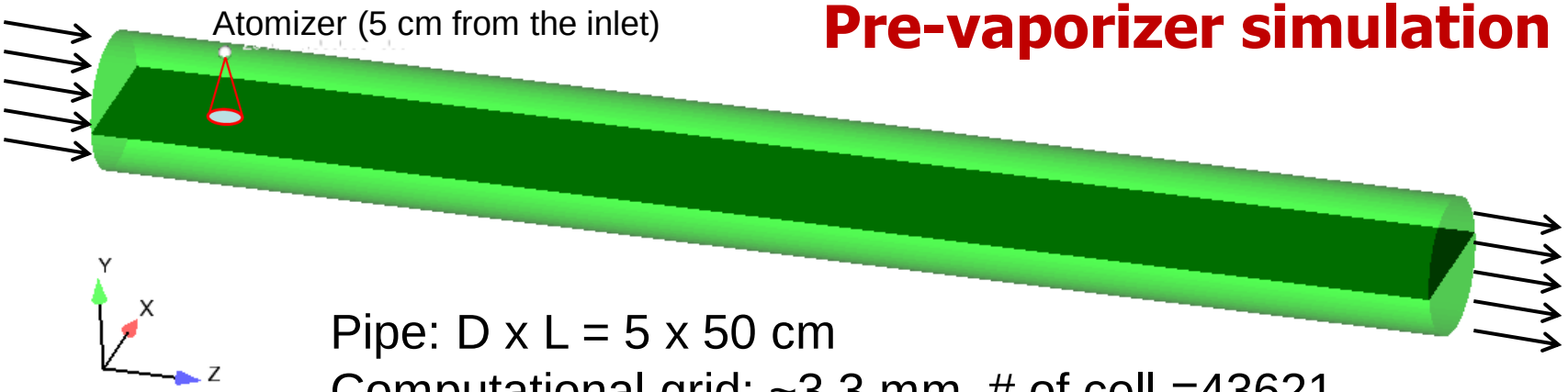
Expt: Vanderover, 2008





F-76 Model application

Pre-vaporizer simulation



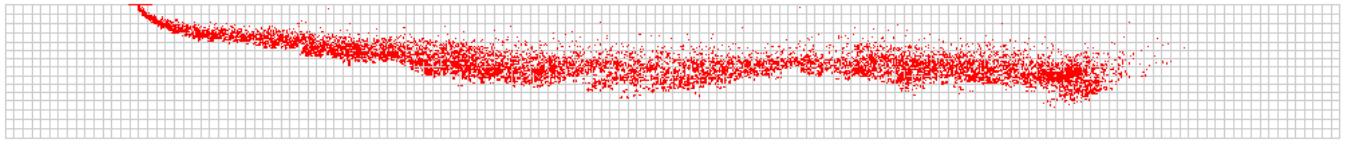
Pipe: D x L = 5 x 50 cm

Computational grid: ~3.3 mm, # of cell =43621

Fuel: F-76

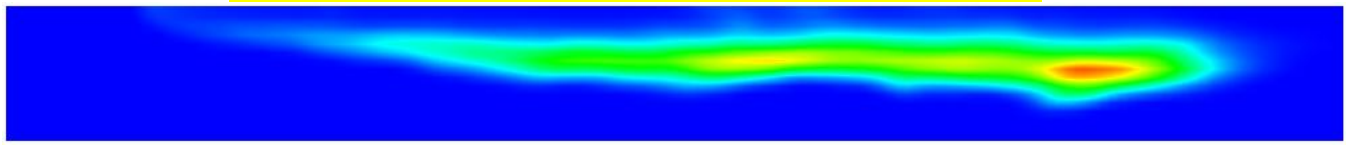
Components	mass fraction
mch	0.047123
c8h16	0.017564
ic10h22	0.028789
c10h22	0.052278
mcymene	0.022761
c10h18	0.004615
c12h18	0.022761
c11h16	0.024808
tetralin	0.015839
c12h26	0.020146
c10h8	0.005592
c13h28	0.013004
ic16h34	0.234979
c14h30	0.005729
c16h34	0.195880
c18h38	0.144496
c14h10	0.008782
c20h42	0.093282
c21h44	0.041573

Drop distribution



@ 10 ms asoi

Fuel mass fraction distribution



For a given injection amount, to determine

- Air mass flow rate
- Inlet air temperature (heated air < 250 C)
- Drop size (SMD)

Summary and Conclusions

- A surrogate model for physical properties of F-76 fuel was developed and validated against measured data.
- Automation of the modeling process is in progress.
- The surrogate fuel model is being used to help determine experimental conditions.
- Extending group chemistry representation, physical surrogate components were considered in combustion chemistry using generic reaction pathways.
- Performance of the PSGCR model was tested for ignition delay times prediction.

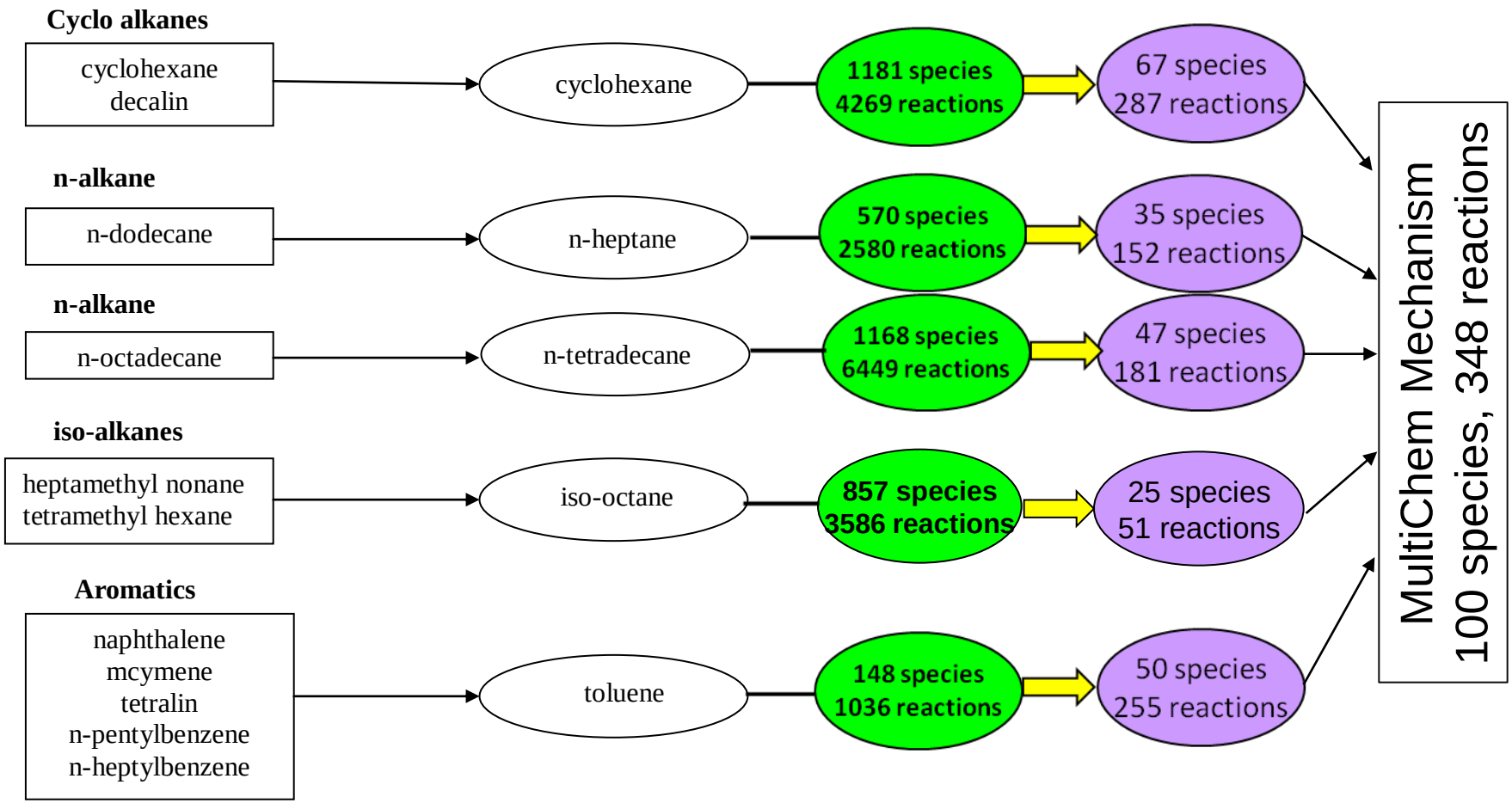
Future work

- Further development of reaction mechanisms for heavy olefins and naphthenes, as well as heavy alcohols.
- Improvement and validation of the automatic surrogate builder.
- Modeling of HCCI engine ignition experiments (Task 2) using PSGCR combustion model.
- Modeling of spray ignition experiments (Task 2) will be performed
- CFD simulation of engine combustion/spray behavior.

Thank you!

Questions?

Group Chemistry Representation (GCR) model



Physical surrogates → (PSC)

Chemistry surrogates → (CSC)

Detailed mechanism

ERC reduced mechanism*

* Ra and Reitz, Combustion & Flame 2011

Group Chemistry Representation (GCR) model